Schroedinger equation in position basis

Review

We have the general form of the Schroedinger equation which holds in any basis

$$i\hbar\frac{\partial \psi(i,t)}{\partial t} = \sum_{j} \langle i|H|j\rangle \psi(j,t).$$

In the case of two base states and a Hamiltonian with $H_{11} = H_{22} = E_0$ and $H_{12} = H_{21} = -A$, this describes a physical problem where an electron can be near either of two protons and has an amplitude $iA/\hbar$ per unit time to jump between the two positions. The Schroedinger equations are

$$i\hbar\frac{\partial \psi_1}{\partial t} = E_0\psi_1 - A\psi_2$$

$$i\hbar\frac{\partial \psi_2}{\partial t} = -A\psi_1 + E_0\psi_2$$

This led to two new base states with definite energy

$$|+\rangle = \frac{1}{\sqrt{2}}\big(|1\rangle - |2\rangle\big) \quad \text{with energy} \quad E_+ = E_0 + A$$

$$|-\rangle = \frac{1}{\sqrt{2}}\big(|1\rangle + |2\rangle\big) \quad \text{with energy} \quad E_- = E_0 - A$$

We are going to use the ideas and techniques from this example to find the form of the Schroedinger equation in the definite-position basis.

Introduction

The main goal is to get the Schroedinger equation in the definite-position basis. In that basis, the wave function (x,t) is a function of x and t and is what we referred to a couple weeks ago as "the wave function". It's a special case of the general framework that we have already discussed. This version of the Schroedinger equation is the starting point for many nonrelativistic calculations in atomic, molecular, nuclear, and condensed matter physics. (Elementary particle physics is not on the list because it is mostly relativistic and uses quantum field theory as a starting point.) Along the way, we will get a glimpse of how electrons can move so easily in crystals.

We begin by considering an infinitely long line of discrete positions available to the electron. Think of it as a line of protons or atoms or just abstract points. Label these positions with the index i. When the electron is at position i, that is what we will call the base state with label i written | i
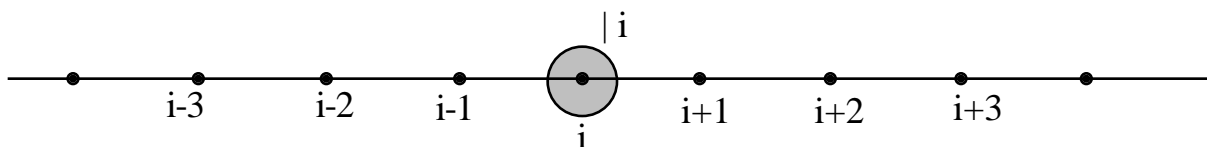
Consider the part of the Schroedinger equation that gives the time derivative of the amplitude to be at position i   (i,t) = i | U(t) |

$$i\hbar\frac{\partial\psi(i,t)}{\partial t} = \sum_j \langle i|H|j\rangle\psi(j,t)$$

$$= ...\langle i|H|i-1\rangle\psi(i-1,t) + \langle i|H|i\rangle\psi(i,t) + \langle i|H|i+1\rangle\psi(i+1,t)...$$

There is an infinite chain of equations like this—one for each value of i. Now we must say something about H. There is an energy that we call E_0 again that is associated with just being at a site, and for now, it is the same for all sites. So i | H | i = E_0. There is also an amplitude that the electron can jump just one step either way. We call this i | H | i+1 = i | H | i-1 = -A. Now the equation for   (i,t) is

$$i\hbar\frac{\partial\psi(i,t)}{\partial t} = -A\psi(i-1,t) + E_0\psi(i,t) - A\psi(i+1,t)$$

If there were no hopping (A = 0), the equations would uncouple and every   (i,t) would have the simple time dependence $e^{-iE_0 t/\hbar}$ so that that the electron would just sit in one place and have energy E_0. But with A   0, the i equation is coupled to the i+1 and i-1 equations. The amplitude at site i changes due to the arrival of electron amplitude from the two neighboring sites. For each i value, there is an equation like the one above, and each is coupled to two others through the hopping terms.

That sets up the problem. Now lets solve it. It's easier than it looks. As usual, we want to know what the stationary states are. So we make the *ansatz* (guess)

$$\psi(i,t) = e^{-iEt/\hbar}a_i$$

(Note that in this *ansatz*, it is the same E for all i.) We put this into the equations and try to find special values of E and the a_i that make it a solution. As in the two-state problem, i$\hbar$ / t becomes E, and all the exponentials cancel to leave us with algebraic equations

$$Ea_i = -Aa_{i-1} + E_0 a_i - Aa_{i+1}$$

These are solved by another *ansatz*

$$a_j = e^{iKj}.$$

(To avoid excessive confusion due to the two meanings of i, I changed the name of i to j.) Put this *ansatz* in the equation above (with i   j) and get

$$Ee^{iKj} = -Ae^{iK(j-1)} + E_0 e^{iKj} - Ae^{iK(j+1)}$$

$$Ee^{iKj} = E_0 e^{iKj} - Ae^{iKj}\left(e^{iK} + e^{-iK}\right)$$

$$E = E_0 - 2A\cos K = (E_0 - 2A) + 2A(1 - \cos K)$$

This is remarkable on several counts. First, it was not that hard to find a solution to what looked like a hard problem in the beginning. Second, there are a lot of solutions: one for each value of K. For each choice of K, we get an energy value given above that is the energy of a stationary state. The allowed values of K are the real numbers between -

and . You can put in some value of K outside that range, but it is just repeating a choice inside. That's because

$$e^{i(K+2\pi)j} = e^{iKj}.$$

The range of values for E is E_0-2A to E_0+2A. You should make a graph of E vs. K. Third, these wave functions are spread evenly over the whole line of points. The amplitudes for the stationary states labeled with K and with energy E(K) = E_0-2A + 2A(1-cosK) have the variation

$$\psi_K(j,t) = e^{-iEt/\hbar} e^{iKj}.$$

These resemble states of definite momentum more than they resemble states with the electron stuck to some atom. To make that a bit more suggestive, we can label the sites by their position coordinate x_j. If we start at some point and call it j = 0 with position x_0 = 0, and if the spacing between the sites is b, then x_j = jb. Then rewrite the exponent Kj = (K/b) x_j = k x_j = p $x_j/\hbar$ with k K/b and p=$\hbar$k as usual. Thus the spatial part is

$$e^{iKj} = e^{ipx_j/\hbar}.$$

Look at the energy for small K.

$$E \quad (E_0 - 2A) + AK^2 = (E_0 - 2A) + \frac{Ab^2}{\hbar^2}p^2$$

The usual expression for the contribution of the kinetic energy to the total energy is p²/(2m). So at small momentum, the electron is behaving like it has a mass m=$\hbar^2$/(2Ab²) or Ab²=$\hbar^2$/(2m).

Even though there are all those atoms to bump into, the electron can still travel along the line with definite momentum. This observation is the foundation of a great deal of solid state physics. It can be pushed a little farther to give an understanding of the relationships between conductors, insulators, and semiconductors. (We won't do that now. Something needs to be left for 9HE.)

Now let's continue on the path toward the x-basis Schroedinger equation. Back up to the point where we had

$$i\hbar\frac{\partial\psi(j,t)}{\partial t} = -A\psi(j-1,t) + E_0\psi(j,t) - A\psi(j+1,t)$$

and switch to using position x_j instead of j. Also generalize a little by allowing E_0 to become a function of position. Change notation as follows

$$j \quad x_j \quad j \pm 1 \quad x_{j\pm1} = x_j \pm b$$

$$\psi(j,t) \quad \psi(x_j, t) \qquad\qquad ,$$

$$E_0 \quad E(x_j)$$

so that the Schroedinger equation becomes

$$i\hbar \frac{\partial \psi\left(x_j, t\right)}{\partial t} = E\left(x_j\right)\psi\left(x_j, t\right) - A\left[\psi\left(x_j + b, t\right) + \psi\left(x_j - b, t\right)\right]$$

$$= \left[E\left(x_j\right) - 2A\right]\psi\left(x_j, t\right) - Ab^2 \frac{1}{b^2}\left[\psi\left(x_j + b, t\right) - 2\psi\left(x_j, t\right) + \psi\left(x_j - b, t\right)\right]$$

The last step is to take the limit b → 0 so that the line of discrete points makes a better and better approximation to the continuous line. In that limit, the term in the {} brackets becomes the second derivative of ψ with respect to x. (To see that, think of the second derivative as the derivative of the first derivative and use the definition of the derivative as the limit of the change in the function divided by the change in the argument twice.) We can choose E(x) and A as we please. Adjust A so that in the b → 0 limit Ab² → ℏ²/(2m) with m the mass of the electron as was the case for finite b but small momentum. Adjust E(x) so that in the limit b → 0,
E(x) - 2A → V(x) with V(x) a function of x that is finite in the limit. Assemble the pieces to get

$$i\hbar \frac{\partial \psi\left(x, t\right)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi\left(x, t\right)}{\partial x^2} + V\left(x\right)\psi\left(x, t\right).$$

That's it! It's the Schroedinger equation in the position basis for a particle moving on a line. The interpretation of the terms follows from a review of the derivation. The left hand side is associated with the total energy. The first term on the right hand side is the kinetic energy. (Notice that with the identification p = -iℏ ∂/∂x that we had a hint of before, the second derivative term is [p²/(2m)]ψ.) The second term on the right hand side is the potential energy *i.e.* a contribution to the energy that varies with position.

To find the stationary states, use the old *ansatz*

$$\psi_E\left(x, t\right) = e^{-iEt/\hbar}\psi_E\left(x\right)$$

to look for a state with definite E. When put in the Schroedinger equation this gives

$$E\psi_E\left(x\right) = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi_E\left(x\right)}{\partial x^2} + V\left(x\right)\psi_E\left(x\right).$$

This is called the time-independent Schroedinger equation. It determines the allowed values of E. The solutions ψ_E(x) give the spatial dependence of the wave functions with definite energy E.